AT

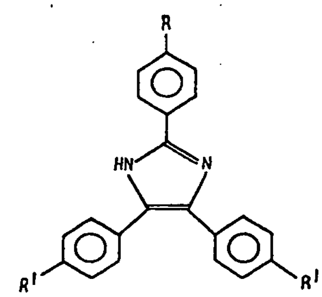
(12) UK Patent Application (19) GB (11) 2 004 380 A

(21) Application No. 7837354
(22) Date of filing 19 Sep 1978
(23) Claims filed 19 Sep 1978
(30) Priority data
(31) 834587
(32) 19 Sep 1977
(33) United States of America (US)
(43) Application published 28 Mar 1979
(51) INT CL[2] G03C 1/76
(52) Domestic classification G2C C13 C19A C4B2 L1D3D L1F
(56) Documents cited None
(58) Field of search G2C

(71) Applicant
Eastman Kodak Company
343 State Street, Rochester, New York 14650, United States of America
(72) Inventors
Steven Roy Levinson
Anthony Adin
(74) Agents
L. A. Trangmar B.Sc., C.P.A.

(54) Heat-bleachable composition useful in photography

(57) A heat-bleachable composition comprising a hexaarylbii midazole, preferably an oxidative dimer of a compound of the formula:



wherein each of R and R' represents a hydrogen atom or an alkyl group having up to 4 carbon atoms, and a dye, preferably a formazan dye or a metal complex thereof, which is bleached upon reaction with a product formed on heating the hexa arylbii midazole can be used to form either a thermographic layer or a heat-bleachable filter or antihalation layer which is very suitable for inclusion in a heat-processable photographic material. Such a photographic material may, for instance, contain a photographic silver halide and a reducing agent therefor, or a vesicular recording layer.

GB 2 004 380 A

SPECIFICATION

Heat-bleachable composition useful in photography

The present invention relates to a heat-bleachable composition useful in photography.

Photographic materials are known which can be processed, after imagewise exposure, simply by heating. These materials include those known alternatively as heat-developable or photothermographic materials. It is desirable for heat developable materials, especially photographic films, to have an antihalation or filter layer particularly if intended for microimaging, and for this layer to be bleached by the heat-processing procedure. Heat-bleachable antihalation layers which have already been proposed for heat-processable photographic materials include a layer containing an acid component of a dye which is neutralized by a heat generated base as described, for instance, in U.S. Patent 3,769,019. A problem with this type of antihalation layer is that the decolourized form of the dye is not always as permanent as desired. Antihalation layers containing photobleachable dyes are also known but may be disadvantageous, through requiring a post-process light bleaching step.

A layer useful as an antihalation or filter layer in a photothermographic material, may also be useful alone for thermographic imaging. For example, imagewise bleaching of a formazan dye by heating in the presence of a reducing agent is known (see *Research Disclosure*, October 1974, Item 12617, pages 12–30).

According to the present invention there is provided a sheet material which comprises a support and incorporated in the support or in a layer or layers coated on one side thereof a hexaarylbiimidazole and a dye which is bleached upon reaction with a product formed on heating the hexaarylbiimidazole.

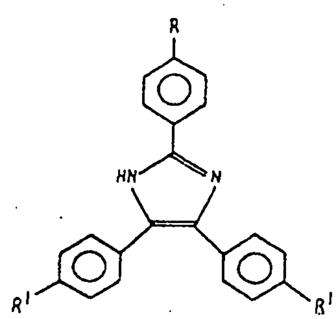
The material is preferably a sensitive photographic material comprising a photosensitive layer, the hexaarylbiimidazole, and the antihalation or filter dye being such that at least 40%, and preferably at least 90%, of the dye is bleached within less than 20 minutes, typically within 30 seconds, when the material is heated to a temperature of at least 90°C, and often of at least 120 or 130°C. An antihalation or filter component of the invention is advantageous because it has a good shelf-life, is bleached at a satisfactory speed on heating, and, once bleached, has good stability, there being little tendency for unwanted stain to form on keeping.

A thermographic material of the invention may comprise a support having thereon at least one layer comprising at least one hexaaryl biimidazole, at least one dye, preferably a formazan dye, that is reactive with the product formed upon heating the hexaaryl biimidazole to a temperature of at least about 90°C and a binder, the optical density due to the dye or dyes, at the absorption maximum being reduced by at least 40% and preferably by at least 90% within less than 30 seconds upon heating the material to a temperature of at least 120°C.

A variety of hexaaryl biimidazole compounds are useful in a photographic material according to the invention. These hexaaryl biimidazole compounds which may be described as oxidative arylimidazolyl dimers, are known compounds and can be prepared by methods known in the art. For instance, hexaaryl biimidazoles can be prepared by means of an interfacial oxidation of the parent triarylimidazole using potassium ferricyanide as an oxidant. Typical hexaarylbiimidazole compounds that are useful according to the invention are described, for example, in and can be selected from the following U.S. Patents: 3,734,733; 3,390,997; 3,383,212; 3,445,234; 3,395,018; 3,390,994; 3,615,481; 3,666,466; 3,630,736 and 3,533,797.

Typical examples of useful hexaarylbiimidazole compounds include oxidative 2,4,5-triaryl imidazolyl dimers in which the aryl groups are selected from *p*-isopropylphenyl, *p*-methoxyphenyl, *p*-n-butylphenyl, *p*-methylphenyl, and *p*-ethylphenyl.

An especially useful compound is an oxidative arylimidazole dimer of a compound represented by the formula:



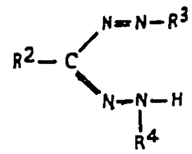
(I)

wherein R and R′ are alkyl containing 1 to 4 carbon atoms or hydrogen.

If desired, a mixture of hexaarylbiimidazole compounds can be used, for example a mixture of two compounds of Formula (I), R and R′ being hydrogen in one compound and isopropyl in the other.

A variety of dyes can be used for heat-bleachable materials of the invention. An antihalation layer preferably has substantially uniform absorption in the spectral region in which the imaging composition is sensitive. Formazan dyes and azo dyes are examples of dyes that are useful.

Especially useful antihalation dyes are formazan dyes, for example, those of the structure:



formazan dye

wherein

R^2 is alkyl or aryl, such as methyl, ethyl, hexyl or phenyl, *p*-nitrophenyl, and dimethoxyphenyl;

R^3 is aryl, preferably phenyl, including substituted phenyl, such as *p*-nitrophenyl, *p*-methoxyphenyl and anthraquinonyl; and

R^4 is aryl, preferably phenyl, including substituted phenyl, *p*-nitrophenyl, *p*-methoxyphenyl and anthraquinonyl.

Especially useful formazan dyes includes, for instance:

1. 1, 3, 5—triphenylformazan
2. 1— (4—chlorophenyl) —3, 5—diphenylformazan
3. 1—p—nitrophenyl—3, 5— (diphenyl) formazan
4. 1, 5—diphenyl—3—methylformazan
5. 1, 5—diphenyl—3— (3—iodophenyl) formazan
6. 1, 5—diphenyl—3— (2—naphthyl) formazan, and
7. 1— (2—carboxyphenyl)—3, 5—diphenylformazan.

Other useful formazan dyes are described, for example, in *Research Disclosure*, October 1974, Item 12617, pages 12–30.

Mixtures of formazan dyes can be especially useful to provide the desired degree of absorption. An example of a mixture of formazan dyes is triphenylformazan with 1-(*p*-nitrophenyl)-3-methyl-5-phenylformazan.

The formazan dyes and their preparation are known in the art: see, for example *Chemical Revisws*, 1955, beginning at page 356.

The coverages and proportions of the components of a heat-bleachable material of the invention can vary over wide ranges. For example, in some thermographic uses, the concentration of dye is sufficient to provide an optical density of at least 0.05. For antihalation purposes it is desirable that the concentration of the dye be sufficient to provide an optical density of at least 0.2 such as from 0.3 to 0.8. The hexaaryl biimidazole should be present in at least sufficient concentration to provide at least 40% bleaching of the described dye. With formazan dyes, for example, a useful concentration is within the range of 0.2 to 10 moles of the hexaaryl biimidazole per mole of the dye. Typically, an excess of the hexaaryl biimidazole compound ensure the desired degree of bleaching.

The preferred molar ratio of hexaaryl biimidazole compound to dye is within the range 0.4 to 3.0:1, especially preferred values being in the range 1.0 to 1.5:1.

The exact mechanism by which the dye in the sheet material of the invention is bleached when the material is heated is not known but it is believed that the hexaaryl biimidazole compound decomposes to form radicals which react with the dye.

Sheet materials according to the invention can contain various colloids and polymers alone or in combination as binders in the layer or layers present. Suitable binders may be hydrophilic or hydrophobic and include, for example, proteins such as gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as detran and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinyl pyrrolidone) and acrylamide polymers. Other synthetic polymeric compounds which can be useful include dispersed vinyl compounds for instance in latex form. When a formazan dye is used with a hexaaryl biimidazole for antihalation purposes, a useful binder is a polysulphonamide, for instance a poly(ethylene-co-1, 4-cyclohexylenedi methylene-1- methyl-2, 4-benzene disulphonamide) binder. Also, water-insoluble polymers, such as poly(vinyl butyral) (e.g. 'BUTVAR B-76', trade mark, a product available from the Monsanto Company, U.S.A.) and latexes which are compatible with the antihalation or filter compounds are useful.

An antihalation or filter layer in accordance with the invention can be useful in a variety of photographic materials including those which are designed to provide an image from photographic silver halide, such as a colour image, and materials designed for non-silver imaging, such as diazotype and vesicular materials. Photographic materials which are intended for microimaging benefit particularly from the antihalation compositions according to the invention.

The hexaaryl biimidazole compound and dye can be in any location in a material of the invention which allows bleaching of the dye upon heating. For antihalation purposes, they may usefully be in a layer (or

3NSDOCID: <GB 2004380A I >

group of adjacent layers) between the photosensitive layer and the support, in the support itself or, if the support is transparent, in a layer (or group of adjacent layers) coated on the side of the support opposite to that carrying the photosensitive layer. Other components of an imaging material according to the invention can be any location in the material which allows formation of the desired image. For example, one or more components of the imaging material can be in one or more layers thereof. Thus, it can be desirable to include certain percentages of the components in a protective over layer of a heat-developable material. In some cases doing so can reduce migration of addenda between the layers of the material.

The heat developable photographic recording materials according to the invention comprise a photosensitive component which can be either a silver or a non-silver component. When a silver photosensitive component is used, a photographic silver halide is preferred because of its high photosensitivity. A typical coverage of photosensitive silver halide in a heat developable photographic material according to the invention is from 1×10^{-4} to 0.1 mole per square metre. Preferred photographic silver halides are silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, or mixtures thereof, but silver iodide is also useful. Very fine grain photographic silver halide is preferred although coarse or fine grain photographic silver halide can be used if desired. The photographic silver halide can be prepared by any of the procedures known in the photographic art, especially procedures for the preparation of gelatino-silver halide emulsions. Useful preparative procedures and forms of photographic silver halide suitable for purposes of the invention are described, for example, in the *Product Licensing Index*, Vol. 92, December 1971, Item 9232, and on page 107. *Research Disclosure*, Vole 148, August 1976, Item 14879, and Vol 125, September 1974, Item 12537. Heat-processable silver halide-containing compositions include those which contain a silver halide developing agent and a development activator, or activator precursor, and those which contains a reducible organic silver salt and a reducing agent therefor.

A variety of non-silver photosensitive components can be useful in photographic materials of the invention. Especially useful photosensitive components are those designed for microimagining purposes.

Silver halide-containing heat-developable photographic materials of the invention can comprise a variety of reducing agents and precursors thereof, especially organic reducing agents which are typically photographic silver halide developing agents. These reducing agents can be useful in combination. Developing agents which are especially useful are polydydroxybenzenes; aminophenol reducing agents; ascorbic acid and its derivatives, hydroxylamines; 3-pyrazolidones; reductones; gallic acid esters; sulphonamidophenols such as described in *Research Disclosure*, Vol 105, January 1973 Item 10513 and phenylenediamine silver halide developing agents.

An imaging material according to the invention can contain an image toner to provide a more neutral tone image upon processing.

It is often useful to include one or more melt-forming compounds in an imaging material according to the invention, for instance in the imaging layer and/or in an antihalation layer or filter layer. A melt-forming compound is a compound which provides at the processing temperature a reaction medium which permits the reaction components to interact more readily. Typically useful melt-forming compounds are amides, imides, cyclic ureas and triazoles which are compatible with the other components present in the sensitive material. Melt-forming compounds are described, for example in *Research Disclosure*, Vol 150, October 1976, Item 15049.

Spectral sensitizing dyes or dye combinations are useful in the imaging materials and compositions of the invention. Suitable dyes are described, for example, in the *Product Licensing Index*, Vol. 92, December 1971, Item 9232.

The silver-containing imaging materials according to the invention can have a range of pAg values, typically from 2 to 13. the pAg can be conveniently measured using conventional calomel and Ag-AgC1 electrodes, connected to an 'Orion' digital pH mater.

The imaging materials according to the invention typically are acidic, normally having a pH of from 2 to 6, and preferably 3.5 to 5.0. The combination of the biimidazole and dye is also preferably acidic.

A sensitive silver-containing material of the invention may contain a stabilizer or stabilizer precursor to improve post-processing image stability. Typically useful stabilizers or stabilizer precursors are sulphur-containing compounds which form a stable silver mercapide upon heating in the heat developable photographic material. Useful stabilizers or stabilizer precursors include, for instance, those described in United Kingdom Patent Specification 1,346,252. Photolytically activated polyhalogenated organic compounds as described, for example, in U.S. Patents 3,874,946, and 3,707,377 may be used.

A development activator (also known as an alkali-release agent, base-release agent or an activator precursor) can be useful in a silver halide imaging material of the invention. Suitable development activators are described, for example, in Belgian Patent 709, 967 and *Research Disclosure*, Vol 155, March 1977, Item 15567. Useful activator precursors include guanidinium compounds such as guanidinium- trichloroacetate, diguanidinium glutarate, succinate and malonate; quaternary ammonium malonates; amino acids, such as 6-aminocaproic acid and glycine; and 2-carboxy carboxamide activator precursors.

It may be useful to have an overcoat layer on an imaging material of the invention to reduce fingerprinting and abrasion marks. The layer can be made from a polymer as described above for use as a binder, or from other polymeric materials such as cellulose acetate and polyvinyl chloride.

Imaging materials of the invention especially those which contain a photographic silver halide, can contain other addenda such as development modifiers that function as speed-increasing compounds, hardeners,

plasticizers and lubricants, coating aids, brighteners, antistatic agents or layers and antifoggants. These are described, for example, in the *Product Licensing Index*, Vol. 92, December 1971, Item –232.

The imaging materials according to the invention can comprise any support which can tolerate the processing temperature to be employed. Typical supports include cellulose ester film, poly(vinyl acetal) film, poly(ethylene terephthalate) film, polycarbonate film and polyester film supports as described in U.S. Patents 3,634,089 and 3,725,070.

The antihalation composition comprising the bleachable dye, especially a formazan dye, and the hexaaryl biimidazole can be incorporated in a transparent support such as a cellulose triacetate or polyester film support if desired.

In some cases it is useful to have a small concentration, typically up to 6.5 milligrams, of 1-naphthoic acid per square metre of support in the combination containing the biimidazole compound. The presence of the 1-naphthoic acid reduces undesired release of volatile components from the combination. Other acids that are useful include 2-naphthoic and benzoic acids. Election of a suitable 2-napthoic and benzoic acids. Selection of a suitable binder can influence the desirability of the addition of a separate acid compound.

An especially useful embodiment of the invention is a photographic material comprising a support having thereon at least one silver halide photosensitive layer, and at least one antihalation layer comprising, with the hexaaryl biimidazole, a formazan antihalation dye, and a polymeric binder comprising a maleic anhydride-styrene copolymer.

A variety of imagewise exposure means are useful exposing sensitive materials according to the invention. These materials are typically sensitive to the ultravoilet and blue regions of the spectrum, unless containing a spectral sensitizing dye. Suitable means include tungsten lamps, lasers and electron beams. In the case of thermographic materials of the invention, any convenient means can be used for imagewise heating.

A visible image can be developed, and the antihalation or filter dye bleached, in a heat-developable photographic material according to the invention within a short time after imagewise exposure merely by uniformly heating the material to a temperature within the approximate range of 90 to 250°C, often within the range of 110 to 200°C. This heating time is typically within the range of 1 second to 20 minutes, a maximum of 90 seconds being normal.

The silver halide-containing heat-developable photosensitive materials according to the invention can be useful for forming a negative or a positive image. The kind of image obtained can depend, for example, primarily upon the selection of the particular photosensitive silver halide which can be of negative or direct-positive type.

A variety of heating means can be used in processing a heat developable photographic material of the invention including, for instance, a hot plate, iron or roller, and infrared heating means.

Due to the limited solubility of some compounds, it is often necessary to use organic solvents to aid in the preparation of coatings when making a sheet material according to the invention. Typical organic solvents which can be useful in preparing a composition for coating as an antihalation layer or filter layer according to the invention are tetrahydrofuran, methylene chloride, acetone and butanol.

The following examples are included for a further understanding of the invention.

Example 1

The oxidative dimer of 2,4,5-triphenyl imidazole, prepared according to the procedure described in the *Journal of Organic Chemistry*, *36*, page 2265 (1971), (also known as a lophine dimer) (35 mg) was dissolved in 1 gram of tetrahydrofuran. To the resulting composition was added 2 grams of a 20% by weight acetone solution of the polysulfonamide: poly(ethylene-*co*-1, 4-cyclohexylene dimethylene- 1-methyl-2, 4-benzene disulphonamide). Seven milligrams of 1,5-diphenyl-3- (para-methoxyphenyl) formazan dye was dissolved in this solution. The resulting dye solution was coated on a poly(ethylene terephthalate) film support at a 0.15 mm wet coating thickness with a doctor blade. The resulting coating was permitted to dry to provide a heat bleachable material according to the invention. This material bleached rapidly and completely upon heating by contacting with a hot metal block at 150°C for a few seconds. The measure of the activation enthalpy was made from bleach rates at 90°C and 112°C and was approximately 29 kilocalories per mole.

Example 2

The procedure of Example 1 was repeated using a methylene chloride solvent in place of tetrahydrofuran. The dye-containing composition was coated at a 0.05 mm wet coating thickness on a poly (ethylene terephthalate) film support. The dye-containing composition was coated on the support at the following coverage:

oxidative dimer of 2, 4, 5—triphenylimidazole	4.8 mg/dm^2
triphenylformazan dye	1.1 mg/dm^2
binder (as described in the following Table I)	21.5 mg/dm^2

The following results were obtained with the noted polymers as described in Table I.

TABLE I

Binder Polymer	Absorbance at λ_{max}	Absorbance after 10 sec. 160°C Bleach at λ_{max}	Absorbance after 10 sec. 160°C Bleach at 400 nm
poly (vinylbutyral)	0.78	0.04	0.08
poly [4, 4'—isopropylidenediphenylene isophthalate-coterephthalate (50 : 50)]	1.60	0.08	0.11

The materials were incubated at 38°C at 50% relative humidity. The results indicated a minumum loss of dye density and no significant impairment of bleaching even after 3 weeks incubation. Incubated, pre-bleached samples also showed no colour-return after 3 weeks at the described incubation conditions.

Example 3

The procedure described in Example 2 was repeated using the described polyester binder with the concentration of the components in the coating as follows:

oxidative dimer of 2, 4, 5—triphenyl-imidazole	5.4 mg/dm^2
triphenylformazan dye	3.2 mg/dm^2
polyester binder (as described in Example 2)	21.5 mg/dm^2
p—toluenesulphonic acid	1.1 mg/dm^2

The coating was heated as described in Example 2. No volatiles were observed to be released from the coating containing the described acid upon heating as described at 160°C for 10 seconds.

Example 4

A tetrahydrofuran formulation was prepared similar to that described in Example 2 with coatings containing:

triphenylformazan dye	1.1 mg/dm^2
polysulphonamide binder	21.5 mg/dm^2

The molar ratio of the oxidative imidazole dimer to the dye was varied between 0.5 mole of dimer per mole of dye and 2.75 moles of dimer per mole of dye in 0.25 mole increments. The results were compared to unbleached coatings. The results indicated that an optimum level for the particular formulation was about 1.6 moles of the described dimer per mole of dye. This provided excellent bleaching properties for the coating when heated for 5 seconds at 160°C. It also provided excellent bleaching properties when the coating was heated at 150°C for 10 seconds. The bleaching properties of the coating were good at 140°C when it was heated for 10 seconds but less good when the coating was heated at 130°C for 10 seconds.

Example 5

A tetrahydrofuran formulation similar to that described in Example 2 was prepared containing the following:

triphenylformazan dye	1.1 mg/dm^2
oxidative imidazole dimer (as described in Example 2)	3.4 mg/dm^2

A polysulphonamide binder was mixed with the formulation at concentrations from 50 to 400 mg/ft^2 (corresponding to 5.4 to 43.1 mg/dm^2) in varying increments.

It was found that after incubating the resulting coatings at 38°C and 50% relative humidity for 4 weeks that more dye was lost on incubation with lower polymer levels. Upon incubation the polymer coverage of 37.7 mg/dm^2 exhibited less than 20% dye loss in 4 weeks and about 10% dye loss in 2 weeks. Changes in formulation may provide different stability correlations.

Example 6

A tetrahydrofuran formulation was prepared similar to that described in Example 5 containing the following:

triphenylformazan dye	1.1 mg/dm^2
oxidative imidazole dimer	3.8 mg/dm^2
polysulphonamide binder (as described in Example 1)	32.3 mg/dm^2

The following acids at coverages of 2.5, 5, 10 and 20 mg/ft^2 (corresponding to 0.2, 0.46, 0.93 and 1.87 mg/dm^2) were also added to the formulation prior to coating on a support as described in Example 5:

p–toluenesulphonic acid

1—naphthoic acid

After incubation the results demonstrated that low coverages (5 mg/ft^2) of 1—naphthoic acid appeared to provide less dye loss on incubation, slightly increased processing rate, and did not affect the stain observed after bleaching of the resulting coating.

Example 7

A tetrahydrofuran formulation was prepared similar to that described in Example 5 containing the following components:

triphenylformazan dye	1.1 mg/dm^2
oxidative imidazole dimer	5.4 mg/dm^2
polymeric binder consisting of copoly (maleimide-styrene) (50:50 parts by weight) (available as 'Lytron 820' from Monsanto Company, U.S.A. 'Lynton' is a trademark)	21.5 mg/dm^2

The formulation was coated on a support and then heated. The coating provided clear bleaching to a colourless material with no visible evolution of volatile components.

Example 8

This is a comparative example.

Using a tetrahydrofuran formulation similar to that described in Example 5, coatings were prepared containing the following components:

triphenylformazan dye	1.1 mg/dm^2
oxidative imidazole dimer (as described below)	3.2 mg/dm^2
polysulphonamide binder (as described in Example 1)	21.5 mg/dm^2

The following imidazole dimers were included individually in the above formulation:

2– (ortho-chlorophenyl) –4, 5– diphenylimidazole dimer

2– (ortho-methoxyphenyl) –4, 5– diphenylimidazole dimer

The above formulation was tested with and without *p*–toluenesulfonic acid as an addenda (at 5 mg/ft^2 corresponding to 0.46 mg/dm^2).

Upon heat processing of the resulting coating after coating the formulation on a suitable support, minimal bleaching was observed in the coating after heating at 200°C for 30 seconds.

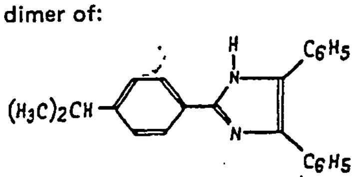
This indicated that the described imidazole dimers are in the above formulation, too stable toward thermal degradation to be optimally useful at the temperature and time used.

Example 9

Certain of the oxidative imidazole dimers have limited solubility in certain solvents. The solubility of certain imidazole dimers is limited to methylenechloride formulations and tetrahydrofuran formulations.

An acetone formuation was prepared by mixing the following components and coating on a transparent poly (ethylene terephthalate) film support:

triphenylformazan dye	1.1 mg/dm^2
solubilized imidazole oxidative dimer of:	4.0 mg/dm^2



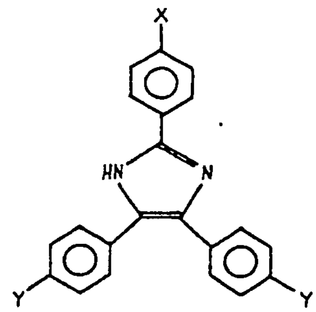
polysulphonamide binder (as described in Example 1)	32.3 mg/dm^2

After the above formulation was coated on a film support, the coating was permitted to dry and then heat processed by heating the material at 160°C for 10 seconds. This provided good bleaching of the coating.

The coating before bleaching was incubated 4 weeks at 38°C and 50% relative humidity. This resulted in a 37.5% loss in dye density with no impairment of bleaching ability at 160°C.

Example 10

Additional imidazole dimers were also included in a heat bleachable layer. These were solubilized imidazole oxidative dimers of compounds within the following formula:



Compound	X	Y
10 A	Isopropyl	H (Mono)
10 B	H	Isopropyl (Bis)
10 C	Isopropyl	Isopropyl (Tris)
10 D	Methyl	H

Coatings were prepared using tetrahydrofuran as a coating solvent at the following levels of components:

oxidative imidazole dimer	3.7 mg/dm^2
triphenylformazan dye	0.93 mg/dm^2
polymeric binder	28.0 mg/dm^2

The polymeric binder was either maleic anhydride- styrene copolymer (available as 'Lytron' 820 from Monsanto Company, U.S.A.) or a polysulfonamide binder (poly(ethylene-*co*-1, 4-cyclohexylene-dimethylene-1- methyl-2, 4-benzendei sulphonamide)). The coating was permitted to dry to provide a material according to the invention. The formulation was coated at a 0.05 mm wet coating thickness on a poly(ethylene terephthalate) film support.

Good bleaching properties of the resulting material were observed when the material was heated at 160° for 10 seconds with both polymeric binders and with each of the described imidazole dimers with a minimal stain seen at an absorption of 400 nanometers.

Better incubation stability properties were observed with the maleic anhydride-styrene copolymer as a binder.

Example 11

The procedure described in Example 10 was repeated with Compound 10 B with the exception that acetone was used in place of tetrahydrofuran. The dimer was found to have excellent solubility in an acetone formulation.

A coating containing this dimer demonstrated excellent bleaching at 160°C when heated for 10 seconds.

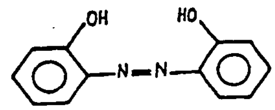
Example 12

The described oxidative, tris-substituted, imidazole dimer (compound 10 C in Example 10) was also included in a formulation in a similar manner to that described in Example 10 using 0.9 mg/dm² of triphenylformazan dye and 28 mg/dm² of the described polymeric binder consisting of maleic anhydride-styrene copolymer. Good bleaching properties were observed when the resulting coating was heated for 10 seconds at 160°C.

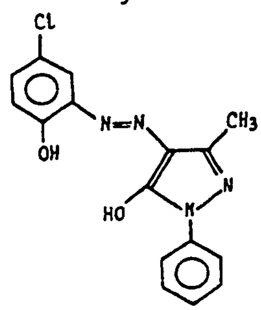
Good results were also observed when the described tris-substituted dimer (Compound 10 C) was coated at higher levels.

Examples 13–16

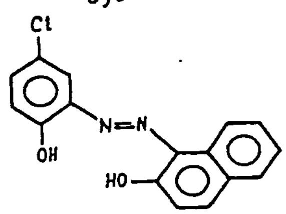
The following dyes were evaluated:



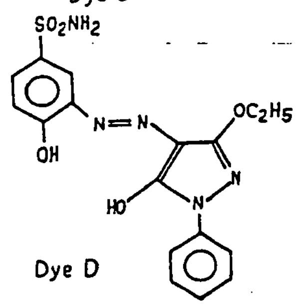
Dye A



Dye B



Dye C



Dye D

Method

Stock solution (A): In 7 grams acetone were dissolved 350 mg 2-phenyl-4, 5-bis(*p*-isopropylphenyl) imidazole dimer.

Example 13

(a) In 0.7 grams stock solution (A) were dissolved 6 mg Dye A (above). To this was added 1.4 grams of 15 weight percent poly(vinyl butryal) ('BUTVAR B-76' available from the Monsanto Co. U.S.A., 'BUTVAR' is a trade mark) in 1:1 acetone:2-methoxyethanol. This solution was coated with a 4-mil doctor blade on subbed poly(ethylene terephthalate) film support.

Example 14

(a) was repeated using 10 mg of Dye B, above.

Example 15

(a) was repeated using 9 mg Dye C above. (A few drops of methyl ethyl ketone were added to help dissolve the dye.)

Example 16

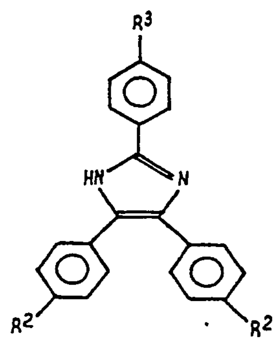
(a) was repeated using 12 mg Dye D, above.

The resulting films were heated by placing the support surface on a 150°C block and the time in seconds to bleach was noted. Diffuse densities were read before and after heat bleaching. The results are given in following Table II

TABLE II

Example No.	Dye	Fresh Density	Bleach Time (Secs.)	Bleached Density
13	A	0.39 (Blue)	20	0.23 (Blue)
14	B	0.91 (Blue	5	0.22 (Blue)
15	C	0.64 (Green)	10	0.18 (Green)
16	D	0.66 (Blue)	15	0.19 (Blue)

The following oxidative triarylimidazole dimers were tested. All dimers were tested in hand coatings with triphenylformazan dye in a polymeric binder. The compounds were oxidative dimers of:



wherein R^2 and R^3 were as defined in following Table III. All substituents are in the para position unless otherwise indicated in Table III.

TABLE III

Example No.	R^3	R^2	Results (10 Sec. at 160°C Bleach)
17	H	H	Good Bleaching
18 (comparative example)	o—chloro	H	Minimal Bleaching
19 (comparative example)	o—methoxy	H	Minimal Bleaching
20	isopropyl	H	Good Bleaching
21	methyl	H	Good Bleaching
22	H	isopropyl	Good Bleaching
23	isopropyl	isopropyl	Good Bleaching
24	methoxy	methoxy	Good Bleaching
25	H	methoxy	Good Bleaching
26 (comparative example)	o—chloro	methoxy	Minimal Bleaching
27	(p—methoxy) (o—methoxy)	p—methoxy	Good Bleaching
28	H	n—butyl	Good Bleaching
29	n—butyl	isopropyl	Good Bleaching
30	H	ethyl	Good Bleaching
31	o—C_5H_{11}	isopropyl	Good Bleaching

Metal chelates of the described formazan compounds are also useful for the purposes described.

Example 32 – Bleaching of a Complexed Formazan Dye

In 0.4 g of warm 2-methoxyethanol was dissolved 2 mg of cupric acetate monohydrate and 6 mg of triphenylformazan to give a dark purple solution. To this solution was added 1.4 g of a 15% by weight solution of poly(vinyl butyral) (BUTVAR B-76) in 1:1 parts by weight acetone/2-methoxyethanol and a solution of 50 mg of the oxidative bis isopropyl substituted triphenylimidazole dimer Compound 10B of Example 10 0.3 g of 1,2-dichloroethane. The resulting solution was coated at a 4 mil wet coating thickness on a poly(ethylene terephthalate) film support containing a subbing layer. The resulting film had a grey-purple colour. A sample of this film having a neutral diffuse density of 0.36 was heated for 5 seconds face-up on a 140°C hot metal block. This caused bleaching of the coating. The neutral diffuse density of the heatd film was 0.09.

Example 33

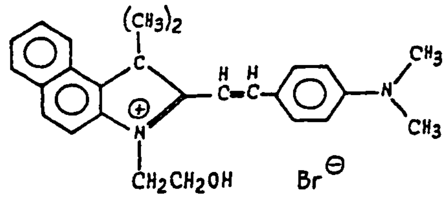
A coating was prepared containing the following materials with a 2 mil doctor blade:

300 mg/ft² 'BUTVAR' B-76 (poly(vinyl butyral))

10 mg/ft² Dye 33A

100 mg/ft² Bis isopropyl substituted oxidative triphenylimidazole dimer (Compound 10B), employing acetone as the solvent.

Dye 33A is represented by the following structure:



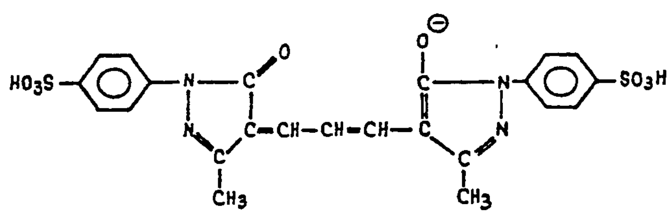
Dye 33A (Polymethine Dye)

Application of heat to this coating (160°C for 10 seconds) resulted in a bleaching of the dye from a density (at λ max) of 0.360 to 0.105 after bleaching (71% change).

Example 34

The procedure described in Example 33 was repeated with the exception that Dye 34B was used in place of Dye 33A.

Dye 34B is represented by the following structure:



Dye 34B (Oxonol dye)

Application of heat to this coating (160°C for 10 seconds) resulted in a bleaching (at λ max = 540) of 0.42 to a density after bleaching of 0.165 (at 61% density decrease).

Example 35 — Use of Melt Formers

A series of low melting solids (i.e. melt formers) were added at 100 mg/ft^2 (~11 mg/dm^2) to the following formulation:

	mg/dm^2
Triphenylformazan	1.1
Bis isopropyl—substituted triphenylimidazole dimer (Compound 10B)	5.4
'LYTRON' 820 (availble from Monsanto Co., U.S.A.) (Purified Monsanto copoly (maleimide/styrene) 50:50)	33

The resulting composition was coated at a 0.05 mm wet coating thickness from acetone solution onto a poly(ethylene terephthalate) film support. A melt former was added to the composition before coating. After drying the coating, it was heated for 5 seconds at 130°C. The results were as follows:

Melt Former	MP (°C)	130°C — 5 sec. Process
None (Control)	—	Minimal Bleach
Methanesulphonamide	91—93	Slight Bleach
Methylurea	99—101	Good Bleach
Resorcinol	109—110	Slight Bleach
N—Methylbenzamide	79—82	Good Bleach

Methylurea- and N-methylbenzamide- contacning coatings can also be processed for 15 seconds at 120°C to bleach the described dye.

Example 36

Coatings were prepared at the same levels as in Example 35 but employing 'BUTVAR' B—76 (poly (vinyl butyral)) instead of 'LYTRON' 820. Processing at a hot block for following times and temperatures produced bleaching of the dye:

Temp. (°C)	Time (sec.)
150	3
140	3
130	5
120	10

Examples 37—47

A series of polymers was tested in a composition as follows:

	mg/dm²
Polymer (see list following)	33
Triphenylformazan	1.1
Bis isopropyl substituted triphenylimidazole dimer (Compound 10B)	5.4

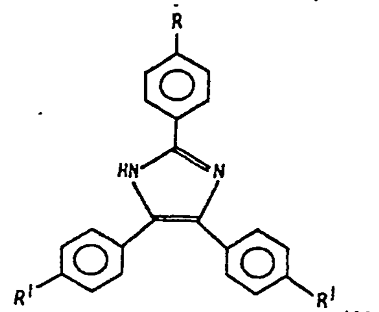
In each instance the coating was heated for 10 seconds at 130°C. The results were as follows:

Example No.	Polymer	Tg (°C)	Solvent	Results at 10 Sec. 130°C Processing
37	poly (N—phenylmaleimide ethylmethacrylate) (comparative example)	159	Methylene Chloride	Minimal Bleach
38	poly (N—phenylmaleimide methylmethacrylate) 25/75 (comparative example)	155	"	Minimal Bleach
39	poly (N—phenylmaleimide n—butylmethacrylate)	105	"	Good Bleach
40	poly (2—hydroxyethyl methacrylate) ('ELVACITE' 2010 a trade mark of E.I. duPont Co., U.S.A.)	100	"	Good Bleach
41	polystyrene (available from Kopper Chemical Co., U.S.A. as 8X)	100	"	Good Bleach
42	poly (N—phenylmaleimide methylmethacrylate) 50/50	170	"	Good Bleach
43	poly (N—phenylmaleimide styrene) 50/50 (comparative example)	220	"	Minimal Bleach
44	poly (N—diphenylmethylmaleimide methylmethacrylate) 50/50 (comparative example)	161	"	Minimal Bleach
45	cellulose acetate propionate (comparative example)	—	Acetone	Minimal Bleach
46	'ETHOCEL' T (ethyl cellulose, a trademark of Hercules Chemical Co., U.S.A.)	—	Acetone	Good Bleach
47	'BUTVAR' B—76 [poly (vinyl butyral) available from Monsanto Chemical Co., U.S.A.]	—	Methylene chloride	Good Bleach

CLAIMS

1. A sheet material which comprises a support and incorporated in the support or in a layer or layers coated on one side thereof a hexaaryl biimidazole and a dye which is bleached upon reaction with a product formed on heating the hexaaryl biimidazole.

2. A material according to claim 1 wherein the hexaaryl biimidazole is an oxidative dimer of a compound of the formula:



wherein each of R and R′ represents a hydrogen atom or an alkyl group having up to 4 carbon atoms.

3. A material according to claim 1 or 2 wherein the dye is a formazan dye or a metal complex thereof.

4. A material according to any of the preceding claims wherein the hexaaryl biimidazole and the dye are incorporated in at least one binder-containing layer coated on the support.

5. A material according to claim 4 wherein the binder in the layer or layers containing the hexaaryl biimidazole and the dye comprises a maleic anhydride-styrene copolymer, a polysulphonamide, or poly(vinyl butyral).

6. A material according to claim 4 or 5 which contains incorporated in the layer or layers containing the hexaaryl biimidazole and the dye benzoic acid, 1-naphthoic acid or 2-naphthoic acid.

~~7. A material according to any of claims 4 to 6 which contains a melt-former~~ incorporated in the layer or layers containing the hexaaryl biimidazole and the dye.

8. A material according to any of the preceding claims which comprises in a layer or layers coated on one side of the support a heat-processable photosensitive composition.

9. A material according to claim 8 wherein the photosensitive composition is coated over a layer or layers containing the hexaaryl biimidazole and the dye.

10. A material according to claim 8 wherein the support is transparent and is coated on one side with the photosensitive composition and on the other with the layer or layers containing the hexaaryl biimidazole and the dye.

11. A material according to any of claims 8 to 10 wherein the photosensitive composition contains a photographic silver halide and a developing agent therefor.

12. A material according to claim 11 wherein the photosensitive composition contains a development activator or a precursor thereof.

13. A material according to any of claims 8 to 10 wherein the photosensitive composition contains a photographic silver halide, a reducible organic silver salt and a reducing agent therefor.

14. A material according to any of claims 1 to 7 which comprises a heat-processable non-silver radiation-sensitive layer.

15. A material according to claim 14 wherein the radiation-sensitive layer is a vesicular recording layer.

16. A coating composition which comprises an organic solvent, a hexaaryl biimidazole, a dye which is bleached upon reaction with a product formed on heating the hexaaryl biimidazole and a binder.

17. A composition according to claim 1 wherein the hexaaryl biimidazole is an oxidative dimer of a compound of the formula of claim 2.

18. A composition according to claim 16 or 17 wherein the dye is a formazan dye or a metal complex thereof.

19. A composition according to any of claims 16 to 18 wherein the binder is a maleic acid-styrene copolymer, a polysulphonamide, or poly(vinyl butyral).

20. A method of making a photographic sheet material which comprises coating a support with a layer of a compmsition according to any of claims 16 to 19.

21. A photographic sheet material made by a method according to claim 20.

22. A method of making a photographic image which comprises heating imagewise a sheet material according to any of claims 1 to 7 which does not comprise a heat-processable photosensitive composition.

23. A method of making a photographic image which comprises exposing imagewise to light a sheet material according to claim 8 or according to claim 8 of any of claims 9 to 15 and heating the material overall to develop the desired image and bring about bleaching of the dye.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon Surrey, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

BNSDOCID: <GB 2004380A I >